Preservation of lipid biomarkers of Fe(III)-reducers and anoxygenic phototrophic Fe(II)-oxidizers during exposure to high pressure and temperature (P/T)

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Background

The rock record is analyzed to search for traces of ancient life on Earth. The fractionation of carbon, sulfur and iron stable isotopes, sedimentary structures, microfossils, as well as molecular fossils (lipid biomarkers), are important indicators for past life. Molecular fossils are persistent compounds that often derive from membrane lipids, recording biological activity in ancient rocks. They provide information on past environmental conditions as well as dominant microbial metabolisms and have been found in sediments as old as 1.6 Ga [1] and 2.5 Ga [2].

So far, molecular fossils have not been detected in Archean Banded Iron Formations (BIFs). The formation of these sediments is still controversial. Most likely, the earliest BIFs were deposited in the absence of significant amounts of oxygen [3,4]. Anoxygenic phototrophic Fe(II)-oxidizing bacteria were suggested being the most plausible mechanism for the deposition of the Fe(III) minerals under anoxic conditions [5]. Moreover, Fe(III)-reducing bacteria might have been involved in iron mineral transformation after deposition, as suggested by Fe and C isotope analyses [6].

Hence, Fe(II)-oxidizing and Fe(III)-reducing bacterial strains were chosen for a systematic biomarker study focusing on the fate of molecules during exposure to high pressure and temperature (P/T).

Current Research and Outlook

We present a new approach investigating the preservation of organic biomolecules of anoxygenic phototrophic Fe(II)-oxidizing and anaerobic Fe(III)-reducing bacterial cells during exposure to diagenetic conditions (P/T) in inert gold capsules. Analysis of fatty acids, alcohols and hydrocarbons was done before and after P/T exposure, with a focus on fatty acids and cyclic terpenoids. We determined how these lipid compounds are affected at increasing temperatures in the absence and presence of iron minerals. In particular, the close association of the iron minerals with the cells appears to have an influence on the stability and preservation of biomarkers. Moreover, in the future we are planning to extend this method to identify carotenoid pigments in the phototrophic Fe(II)-oxidizers and study their preservation.

In summary, the approach of simulating diagenetic and late-stage alteration will help identify stable and source-specific molecular fossils, and elucidate the likelihood of finding diagnostic biomarkers (and thereby evidence) for Fe-cycling bacteria in BIFs and other Fe-rich sediments.

[1] Brocks *et al.* (2005) *Nature* **437**, 866-870. [2] Summons *et al.* (1999) *Nature* **400**, 554-557. [3] Canfield *et al.* (2000) *Science* **288**, 658-661. [4] Bekker *et al.* (2004) *Nature* **427**, 117-120. [5] Kappler *et al.* (2005) *Geology* **33**, 865-868. [6] Johnson *et al.* (2008*) Annu. Rev. Earth Planet. Sci.* **36**, 457-493.

The MAT-253 Ultra — a novel high-resolution, multi-collector gas source mass spectrometer

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We present the design, performance and representative applications of the MAT 253 Ultra – the first prototype of a new class of high-resolution gas source isotope ratio mass spectrometers.

The MAT-253 Ultra is a forward geometry double focusing sector mass spectrometer with a Nier-type gas source. Samples are introduced through capilary bleeds from any of 4 automated flexible bellows and/or a carrier-gas port. Ions enter the analyzer through an adjustable entrance slit (5 to 250 μm). The analyzer has a 23 cm radius magnet and is similar in scale and design to the Neptune Plus MC-ICPMS. The detector array consists of 1 fixed position and 7 moveable positions on 6 trolleys. An RPQ lens is positioned before the central detector position. Each detector position contains both an SEM and faraday cup detector; each faraday can be registered through any of 10 amplifiers varying in gain from 10^7 to 10^{12}.

Ion beams from m/z 1 to ~300 can be collected, with a ~15 % mass range for simultaneous collection. Useful ion yield is ~1 ion per 1200 molecules for CO_2 under standard analytical conditions and using a 250 μm entrance slit. The dynamic range in simultaneously measurable ion currents is ~10^{14}. Backgrounds are negligible in the central detector position when the RPQ is in use, permiting quantitative analysis of low intensity ion beams even with high source pressures. Mass resolving power (M/ΔM, 5%/95% definition) has been measured up to 26,000 and is routinely as good as ~22-24,000 — sufficient to separate most isobaric interferences among isotopologues of H-C-N-O-S molecular species; in particular, it permits separation of ^{13}C from D isotopologues and both from H adducts in alkanes and related organics. Analyzer system stability is routinely < 2ppm/hour, permitting precise analysis of small features on complex peaks. External precision for isotope ratio measurements of relatively intense ion beams are routinely 10's of ppm, relative; measurements of weaker ion beam using SEM detectors reach counting statistics limits down to external precisions of ~0.1 ‰.

The MAT 253 Ultra enables many previously impossible isotopic analyses of gases and volatile organics and their fragment and adduct ions. Demonstrated examples include: $\delta^{13}C$, δD and $^{13}CH_3D$ of methane; $\delta^{13}C$ of propane and many of its fragments (enabling position-specific ^{13}C determination); direct analysis of $\delta^{17}O$ $\delta^{18}O$, $\delta^{15}N$ and ^{15}N-^{18}O 'clumping' in N_2O and its NO fragment; $^{18}O^{17}O$ and $^{18}O_2$ in O_2; and clumped isotope analysis of CO_2 free of contaminant isobaric interferences.